

REMARKS

Cancellation of claims 2-4 renders moot the rejection of these claims.

In response to the Examiner's comments regarding the "less than or equal to 2 mol %" language in the as-filed claims, Applicant has amended claim 1 to recite "greater than zero and less than or equal to 2 mol %," clearly indicating that, in this claim, the range does not include zero. Dependent claim 5, however, recites "less than or equal to 2 wt %" because, as recited in this claim, the range can include zero.

Applicant respectfully traverses the §102(b) rejection over Mizutani, JP '768.

In a solid oxide fuel cell (SOFC) of the present invention, an internal reforming type SOFC, a second solid electrolyte is a solid electrolyte whose "oxide ion conductivity is more than or equal to 0.2 S/cm at 1000°C," which is "scandia-stabilized zirconia containing 9 to 12 mol % of scandia (Sc_2O_3), to which greater than zero and less than or equal to 2 mol % of at least one kind of oxide selected from yttria (Y_2O_3) and ceria (CeO_2) is further added."

The second solid electrolyte of the invention has high oxide ion conductivity, so more oxide ions are supplied to the triple phase boundary of the fuel electrode to promote a cell reaction, and a large amount of water is generated at the fuel electrode. Even if internal reforming is performed under an extremely low s/c ratio, e.g., 0.03 to 0.25, the reforming reaction proceeds independently through water generated by the cell reaction, inhibiting the deposition of carbon on the fuel electrode, and generating stable electric power.

Mizutani '768 discloses a fuel electrode consisting of a cermet of nickel, and scandia-stabilized zirconia (ni-ScSZ). The fuel electrode in the present invention, however, employs a second solid electrolyte which is scandia-stabilized zirconia to

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which at least one kind of oxide selected from yttria (Y_2O_3) and ceria (CeO_2) is added. In addition, the second solid electrolyte of the invention may be further compounded with alumina. Mizutani '768 does not disclose an internal reforming type electrode. This reference does not disclose a second solid electrolyte having the features recited in the claims, and for at least this reason cannot anticipate the present claims.

Applicant likewise traverses the § 103(a) rejection of claims over Mizutani '768 in view of Mizutani '240. The Examiner admits that Mizutani '768 does not disclose all of the features of these claims, e.g., that in the electrolyte material, ScSZ contains yttria, ceria, or alumina.

The Examiner relies on Mizutani '240 for these teachings.

Mizutani '240, however, is not prior art, and hence is not properly combinable with Mizutani '768. Mizutani '240 was published on December 8, 2000, whereas the present application has a priority date of October 23, 2000. In accordance with 37 C.F.R. § 1.55(a), applicant submits herewith an accurate English translation of the priority document. The claim for priority being thus perfected, Mizutani '240 must be withdrawn as a reference. Even if Mizutani '240 were prior art, or if another secondary reference having a disclosure similar to Mizutani '240 were combined with Mizutani '768, that still would not suggest the claimed invention.

Furthermore, Mizutani '768 and Mizutani '240 both include no disclosure of internal reforming in a SOFC. Consequently, even if one of ordinary skill in the art did combine these teachings, which applicant contends would not occur, that still would not result in the invention, as set forth in claims 1 and 5.

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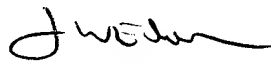
In view of the above amendments and remarks, applicants request reconsideration and allowance of claim 1 and 5.

If there is any fee due in connection with the filing of this Response, please charge the fee to our Deposit Account No. 06-0916.

Respectfully submitted,

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Attachments: Verified English Translation of Priority Document

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TRANSLATOR'S VERIFICATION

I hereby declare and state that I am knowledgeable of each of the Japanese and English languages and that I made and reviewed the attached translation of the certified copy of the Japanese Patent Application No. 2000-322670 filed on October 23, 2000 from the Japanese language into the English language, and that I believe my attached translation to be accurate, true and correct to the best of my knowledge and ability.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, and that such willful false statements may jeopardize the validity of this application or any patent issued thereon.

Date: January 23, 2004

(Signature)

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【Title of the Invention】 SOLID OXIDE FUEL CELL

【Scope of Claims】

【Claim 1】 A solid oxide fuel cell having an electrolyte electrode assembly in which a fuel electrode is connected to one face of a first solid electrolyte showing oxide ion conductivity and an air electrode is connected to the other face, wherein the fuel electrode comprises a cermet of a catalyst and a second solid electrolyte whose oxide ion conductivity is more than or equal to 0.2 S/cm at 1000 °C.

【Claim 2】 The solid oxide fuel cell according to claim 1, wherein the second solid electrolyte is scandia-stabilized zirconia containing 9 to 12 mol% of scandia (Sc_2O_3).

【Claim 3】 The solid oxide fuel cell according to claim 2, wherein the second solid electrolyte is scandia-stabilized zirconia further containing less than or equal to 2 mol% of yttria (Y_2O_3).

【Claim 4】 The solid oxide fuel cell according to claim 2, wherein the second solid electrolyte is scandia-stabilized zirconia further containing less than or equal to 2 mol% of ceria (CeO_2).

【Claim 5】 The solid oxide fuel cell according to claim 2, wherein the second solid electrolyte is a composite material of the scandia-stabilized zirconia and less than or equal to 2 wt% of alumina (Al_2O_3).

【Detailed Description of the Invention】

【0001】

【Technical Field to Which the Invention Pertains】

The present invention relates to a solid oxide fuel cell, more particularly to a solid oxide fuel cell which is used in a distributed power source, a cogeneration system and the like in urban areas, and which is suitable for internal reforming power generation.

【0002】

【Prior Art】

A solid oxide fuel cell (hereinafter referred to as an "SOFC") is a fuel cell in which an oxide ion conductive solid electrolyte is used as an electrolyte. In the SOFC, as the electrolyte is solid, there is no problem of dissipation of the electrolyte, and long life can be expected. Moreover, the operating temperature is as high as about 1000°C, and the utility value of waste heat is high. Furthermore, as output power density is high, it can also be expected to be compact and of high efficiency.

【0003】

Fig. 7 is a view showing a schematic configuration of the SOFC. In Fig. 7, the SOFC 10 has a structure that a fuel electrode 14 and an air electrode 16 are bonded to both faces of an electrolyte 12 to give an electrolyte electrode assembly 18, and both sides thereof are further sandwiched between gas separators 20 and 22. In general, the oxygen ion conductive solid electrolyte such as

yttria-stabilized zirconia (hereinafter referred to as "YSZ") is used for the electrolyte 12. Furthermore, generally, a cermet of nickel and YSZ containing 8 mol% of yttria (Y_2O_3) (hereinafter referred to as "Ni-8YSZ") is used for the fuel electrode 14, and a composite oxide such as lanthanum strontium manganate ($LaSrMnO_3$) is used for the air electrode 16.

【0004】

If hydrogen and air are supplied to the fuel electrode 14 and the air electrode 16 of such SOFC 10, respectively, oxygen ionizes in the air electrode 16 and the oxide ion is transported to the fuel electrode 14 side through the electrolyte 12 because there is a difference between oxygen partial pressure P_1 on the air electrode 16 side and oxygen partial pressure P_2 on the fuel electrode 14 side. Moreover, the oxide ion reaching the fuel electrode 14 reacts with hydrogen to produce water and emit an electron. Therefore, if load 22 is connected to the fuel electrode 14 and the air electrode 16, the free energy change of a cell reaction can be directly taken out as electrical energy.

【0005】

Incidentally, in the SOFC, because of its high operating temperature, it is possible to perform the so-called "internal reforming" in which hydrocarbon, instead of hydrogen, is directly supplied to the fuel electrode to be reformed to hydrogen in a cell body. An internal reforming type SOFC has an advantage of high heat

efficiency since heat generated inside the cell can be utilized for a reforming reaction with great heat absorption. In addition, as an external reforming vessel is unnecessary, there is an advantage of that a fuel cell system may be compact.

【0006】

The reforming reaction of hydrocarbon is a reaction through which hydrocarbon and steam are reacted with each other, and hydrogen and carbon dioxide are ultimately generated. That is, in order to cause a reforming reaction, steam is necessary. If the ratio of steam to carbon in hydrocarbon contained in fuel (hereinafter referred to as an "S/C ratio") is small, unreacted hydrocarbon is directly decomposed at a high temperature and carbon is deposited on the fuel electrode. If carbon is deposited on the fuel electrode, a catalyst is poisoned, which causes a reduction in the output of the SOFC.

【0007】

On the other hand, in the case of the internal reforming type SOFC, usually methane is used as fuel. This is due to the fact that since methane is a chief component of natural gas, it ensures safety, inexpensiveness, and ease in storage and supply as fuel. In general, in the internal reforming type SOFC using methane for fuel, it is said that the S/C ratio of the order of 2 to 3 is necessary in order to inhibit deposition of carbon and to obtain a stable output (for example, see (1) "Solid Oxide Fuel

Cell and Earth Environment" written by Hiroaki Tagawa, AGNE SHOFU PUBLISHING INC., p65, (2) preliminary reports on the fifth symposium lecture on fuel cell, pp.173-177, (3) Abulet Abudula et al., Electrochemistry, vol. 65, No. 10, pp.852-858 (1997)).

【0008】

【Problems to Be Solved by the Invention】

The difference between the open circuit voltage of the fuel cell and the terminal voltage when actually carrying electric current, that is, the magnitude of overvoltage is generally affected by the ohmic resistance of an electrolyte, reaction resistance of a fuel electrode, that of an air electrode or the like. In the case of the internal reforming type SOFC, in addition, as the reforming reaction in the fuel electrode appears as resistance, a reduced catalytic activity of the fuel electrode against the reforming reaction causes an increase in the resistance of the fuel electrode and a reduction in the output power density and the generation efficiency of the SOFC. Thus, to increase the generating performance of the internal reforming type SOFC, it is important to increase the catalytic activity of the fuel electrode.

【0009】

However, conventional Ni-8YSZ generally used as a fuel electrode material has insufficient catalytic activity against the reforming reaction. Therefore, a fuel electrode material with higher activity suitable for

the internal reforming type SOFC is desired.

【0010】

Moreover, to perform stable internal reforming, as described above, a relatively large S/C ratio is necessary. However, excessive addition of steam causes a reduction in the open circuit voltage of the SOFC. Furthermore, excessive addition of steam causes a reduction in SOFC efficiency since it increases auxiliary utility power and necessitates spare energy for steam generation. On the other hand, if the S/C ratio is made small to avoid this, carbon could be deposited and thus the catalyst could be poisoned.

【0011】

Furthermore, when Ni-8YSZ is used as the fuel electrode of the internal reforming type SOFC, its initial property is relatively good. However, Ni-8YSZ has a problem that unless it is operated in a condition of a sufficiently high S/C ratio, catalytic activity is time-coursely degraded when internal reforming operation is continued for many hours and the output power density is reduced.

【0012】

The present invention has an object to improve the power generation performance of a solid oxide fuel cell by improving the catalytic activity of the fuel electrode.

【0013】

Another object of the present invention is to provide

a solid oxide fuel cell in which no poisoning by carbon occurs and stable power generation is possible even when internal reforming is performed under a condition of a low S/C ratio.

【0014】

And yet, another object of the present invention is to provide a solid oxide fuel cell in which the time course degradation of the fuel electrode is reduced when internal reforming is performed and which has excellent durability and reliability.

【0015】

【Means for Solving Problem】

To achieve the objects described above and in accordance with the purpose of the present invention, in a solid oxide fuel cell having an electrolyte electrode assembly in which a fuel electrode is connected to one face of a first solid electrolyte showing oxide ion conductivity and an air electrode is connected to the other face, the fuel electrode comprises a cermet of a catalyst and a second solid electrolyte whose oxide ion conductivity is more than or equal to 0.2 S/cm at 1000°C.

【0016】

If a material having high oxide ion conductivity is used as the second solid electrolyte forming part of the fuel electrode, more oxide ions are supplied to a triple phase boundary of the fuel electrode and a cell reaction is promoted. Hence, even if internal reforming is

performed under a condition of a low S/C ratio, a reforming reaction proceeds independently through water generated by the cell reaction and deposition of carbon on the fuel electrode is inhibited.

【0017】

Moreover, the fuel electrode using the second solid electrolyte having high oxide ion conductivity has higher catalytic activity and less time course degradation than conventional fuel electrodes using YSZ. Thus, if this is used as the fuel electrode of the internal reforming type SOFC, the cell performance, durability, and reliability of the SOFC are improved.

【0018】

【Preferred Embodiments】

In the following, the embodiments of the present invention will be explained in detail. The present invention is characterized in that, in an SOFC having an electrolyte electrode assembly in which a fuel electrode is connected to one face of a first solid electrolyte showing oxide ion conductivity and an air electrode is connected to the other face, a cermet of a catalyst and a second solid electrolyte having high oxide ion conductivity is used as the fuel electrode.

【0019】

Here, for the catalyst constituting part of the fuel electrode, the one having high activity against cell reaction in the fuel electrode is used. Among such

catalysts, specifically, nickel (Ni), cobalt (Co), ruthenium (Ru) or the like are suitable examples. In the present invention, any of the above-mentioned catalysts can be used and there are no specific limitations. The content of the catalyst in the fuel electrode is determined according to the kind of the catalyst employed and the operating conditions of the SOFC or the like so that the triple phase boundary is maintained at the operating temperature of the SOFC and that necessary characteristics such as predetermined electric conductivity and a coefficient of thermal expansion equivalent to the electrolyte are obtained.

【0020】

For the second solid electrolyte constituting another part of the fuel electrode, the one whose oxide ion conductivity is more than or equal to 0.2 S/cm at 1000 °C is used. To further improve the catalytic activity and durability of the fuel electrode, it is particularly preferable that the second solid electrolyte has oxide ion conductivity of more than or equal to 0.25 S/cm at 1000 °C.

【0021】

As for the second solid electrolyte meeting these conditions, scandia-stabilized zirconia (hereinafter referred to as "ScSZ") in which scandia (Sc_2O_3) is solubilized in zirconia is one of the suitable examples. In this case, it is preferable that the scandia content

in ScSZ is 9 to 12 mol%. It is not preferable that the scandia content is less than 9 mol% because the oxide ion conductivity of the fuel electrode is reduced. In addition, it is not preferable that the scandia content is more than 12 mol% because the oxide ion conductivity of the fuel electrode is similarly reduced. It is more preferable that the scandia content in ScSZ is 10 to 11 mol%.

【0022】

Furthermore, the second solid electrolyte may be ScSZ in which only scandia is solubilized or to which yttria (Y_2O_3) or ceria (CeO_2) is further added in a very small amount. If yttria is further added to ScSZ, it is preferable that the content is less than or equal to 2 mol%. It is not preferable that the yttria content is more than 2 mol% because the oxide ion conductivity of the fuel electrode is reduced. It is more preferable that the yttria content is 0.5 to 1 mol%.

【0023】

Moreover, if ceria is further added to ScSZ, it is preferable that its content is less than or equal to 2 mol%. It is not preferable that the ceria content is more than 2 mol% because the oxide ion conductivity of the fuel electrode is reduced. It is more preferable that the ceria content is 0.5 to 1 mol%.

【0024】

Moreover, the second solid electrolyte may be a composite material of ScSZ and alumina (Al_2O_3). If ScSZ

and alumina are compounded, it is preferable that the alumina content is less than or equal to 2 wt% with respect to ScSZ. It is not preferable that the alumina content is more than 2 wt% because the oxide ion conductivity of the fuel electrode is reduced. It is more preferable that the alumina content is 0.5 to 1 wt%.

【0025】

Furthermore, ScSZ may be the one in which one of yttria and ceria is solubilized or in which both of them are solubilized. In addition, alumina may be further compounded with ScSZ in which one or both of yttria and ceria are solubilized.

【0026】

Moreover, the first solid electrolyte may be the one which shows oxide ion conductivity and is not specifically limited. Suitable examples of the first solid electrolyte are, specifically, YSZ in which 8 to 10 mol% of yttria as a stabilizer is added, calcia-stabilized zirconia (CSZ) in which 9 to 12 mol% of calcia (CaO) is added as a stabilizer, ScSZ in which 9 to 12 mol% of scandia (Sc_2O_3) is added as a stabilizer, or the like. In particular, ScSZ is suitable as the first solid electrolyte for the SOFC since it has high oxide ion conductivity.

【0027】

Moreover, the SOFC is generally classified roughly into cylinder, plate and mono block layer schemes, and

the present invention is applicable to all these schemes. That is to say, the shape of the first solid electrolyte is not specifically limited and may be any of cylinder, plate, or honeycomb.

【0028】

Furthermore, for the air electrode, materials which are chemically stable under oxygen atmosphere at high temperatures and which have high electric conductivity are used. As such materials, specifically, the noble metals such as platinum and composite oxides such as LaSrMnO_3 , LaCaMnO_3 , LaMgMnO_3 , LaSrCoO_3 , and LaCaCoO_3 are mentioned as suitable examples. In the present invention, all above-mentioned materials can be employed as the air electrode and are not specifically limited. In addition, the air electrode may be the one which contains only the above-mentioned materials or may be composite materials of the above-mentioned materials and oxide ion conductive solid electrolyte such as YSZ.

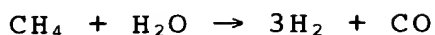
【0029】

Then, the action of the SOFC consistent with the present embodiment will be explained. The reforming reaction of methane is divided into the steam reforming reaction expressed as Chemical Formula 1 and the successive reaction of the water gas shift reaction expressed as Chemical Formula 2. The reforming reaction is an endothermic reaction with great heat absorption and the overall reaction formula is expressed as Chemical Formula

3.

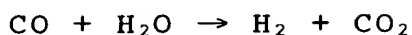
【0030】

【Chemical Formula 1】



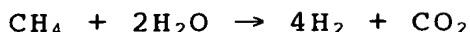
【0031】

【Chemical Formula 2】



【0032】

【Chemical Formula 3】



【0033】

Fig. 1 shows a schematic diagram of the power generating reaction of the internal reforming type SOFC. For example, if a mixed gas of methane whose S/C ratio is 1 and steam is supplied to the fuel electrode 14 of the SOFC 10, the steam reforming reaction of methane expressed in Chemical Formula 1 takes place by the heat energy inside the SOFC 10, and carbon monoxide and hydrogen are generated. The carbon monoxide and hydrogen thus generated are electrochemically oxidized by oxide ions supplied from the electrolyte 12 to give carbon dioxide and steam, respectively, to liberate eight electrons. The electrons thus liberated are supplied to the air electrode side via load not illustrated and are consumed for ionization of oxygen. The power generation of the SOFC 10 is carried out by continuous progress of such a reaction.

【0034】

Here, in the internal reforming power generation of the SOFC 10, the steam reforming reaction of methane appears as the reaction resistance of the fuel electrode 14. In order to cause the steam reforming reaction of methane, as clear from Chemical Formula 1, it is necessary that steam be contained in fuel. Thus, if the S/C ratio in the fuel becomes small, the reaction of Chemical Formula 1 does not proceed to the right. This causes an increase in the reaction resistance of the fuel electrode 14 and a reduction in the output of the SOFC 10.

【0035】

Moreover, according to Chemical Formula 1, if the S/C ratio is at least 1, methane is, thermodynamically, decomposed into carbon monoxide and hydrogen. However, in the actual internal reforming power generation of the SOFC, the conversion ratio of methane does not reach a thermodynamic equilibrium value to leave unconverted methane. Therefore, in a conventional SOFC, to perform a stable internal reforming, it is necessary that the S/C ratio be of the order of 2 to 3 and that steam is excessively added.

【0036】

On the other hand, in the present invention, the second solid electrolyte having high oxide ion conductivity is used as a material for the fuel electrode 14. Therefore, compared with the conventional fuel electrode, more oxide ions are supplied to the triple phase

boundary of the fuel electrode 14. As a result, a cell reaction is promoted and more water is generated in the fuel electrode. Thus, even if fuel having a low S/C ratio is supplied to the fuel electrode 14, the steam reforming of methane is performed by the water generated through the cell reaction and the cell reaction further proceeds due to the hydrogen thus generated.

【0037】

That is to say, the steam reforming reaction of methane proceeds independently by using a material having high oxide ion conductivity for the fuel electrode 14, and the supply of steam does not become a rate-determining process. Moreover, the conversion of methane proceeds with independent progress of the steam reforming, inhibiting the deposition of carbon on the fuel electrode 14 resulting from the direct high temperature decomposition of unconverted methane, and the poisoning of a catalyst as well due to the deposited carbon. Thus, according to the SOFC consistent with the present invention, a high output is obtained in a stable manner even under a condition of very little steam, for example, such as 0.03 to 0.25 of the S/C ratio. In addition, since it is unnecessary to add excessive steam, auxiliary utility power is also less and high generating efficiency is obtained.

【0038】

Furthermore, in a conventional fuel electrode

material, the catalytic activity against the reforming reaction of methane is insufficient, which also causes an increase in the reaction resistance of the fuel electrode 14 and a reduction in the output of the SOFC 10. On the other hand, the fuel electrode 14 using the second solid electrolyte having high oxide ion conductivity has higher catalytic activity against the reforming reaction of methane than the conventional fuel electrodes. Thus, if this is applied to the internal reforming type SOFC, it is possible to obtain the SOFC having excellent generating performance including output density, generating efficiency and the like.

【0039】

Moreover, the conventional fuel electrodes comprising Ni-8YSZ have the problem that the catalytic activity of the fuel electrode shows time course degradation in a case where internal reforming is continued for many hours unless they are operated under a condition of a sufficiently high S/C ratio. On the contrary, if a material having high oxide ion conductivity is used for the fuel electrode, the time course degradation of the catalytic activity against the reforming reaction of methane is inhibited even if they are operated under a condition of a low S/C ratio. Thus, if this is applied to the fuel electrode of the internal reforming type SOFC, it is possible to obtain the SOFC having excellent durability and reliability.

【0040】

Then, a description will now be given to the manufacturing method of the SOFC consistent with the present invention. First, the first solid electrolyte material showing oxide ion conductivity is molded into a predetermined shape and is sintered at a predetermined temperature. Incidentally, to mold the first solid electrolyte material, an optimum method may be used according to the shape of the SOFC. For example, to mold in a plate shape, any one of the press molding method, the tape molding method and the like may be used. In addition, to mold in a cylindrical or honeycomb shape, any one of the extrusion molding method, the injection molding method and the like may be used. Moreover, for the sintering condition of the first solid electrolyte, an optimum temperature is selected according to its composition.

【0041】

Then, slurry containing the catalyst and the second solid electrolyte is applied to one face of the first solid electrolyte and is sintered to give the fuel electrode. Similarly, slurry containing an air electrode material is applied to the other face of the first solid electrolyte and is sintered to give the air electrode. In addition, a fuel gas introducing means and an oxidizer gas introducing means are attached to the resulting electrolyte electrode assembly to obtain the SOFC. Among the application methods

for the fuel and air electrodes, the screenprinting, doctor blade, brushing, spray, dipping methods and the like are specifically suitable examples, but in the present invention, any of these methods may be used and there are no particular limitations.

【0042】

【Examples】

(Example 1)

An ScSZ sintered body containing various additives was prepared using an ordinary ceramic process and oxide ion conductivity was measured at 800 °C and 1000 °C. In addition, for comparison, an 8YSZ sintered body was prepared and the oxide ion conductivity was measured at 800 °C and 1000 °C. The results are shown in Table 1.

【0043】

【Table 1】

Composition	Conductivity (S/cm)	
	1000 °C	800 °C
(10 mol% Sc_2O_3 - 89 mol% ZrO_2) 99 wt% - Al_2O_3 1 wt% (11S1A)	0.290	0.101
10 mol% Sc_2O_3 - 1 mol% Y_2O_3 - 89 mol% ZrO_2 (10S1Y)	0.304	0.104
10 mol% Sc_2O_3 - 1 mol% CeO_2 - 89 mol% ZrO_2 (10S1C)	0.343	0.130
8 mol% Y_2O_3 - 92 mol% ZrO_2 (8YSZ)	0.160	0.070

【0044】

In the case of the 8YSZ sintered body, the oxide ion conductivity at 1000 °C was 0.160 S/cm and that at 800

°C was 0.070 S/cm.

【0045】

On the contrary, in the case of the ScSZ sintered body having (11 mol% Sc_2O_3 - 89 mol% ZrO_2) 99 wt% - Al_2O_3 1 wt% composition (hereinafter referred to as "11S1A"), the oxide ion conductivity at 1000 °C and 800 °C were 0.290 S/cm and 0.101 S/cm, respectively, which was higher than that of the 8YSZ sintered body.

【0046】

Similarly, in the case of the ScSZ sintered body having 10 mol% Sc_2O_3 - 1 mol% Y_2O_3 - 89 mol% ZrO_2 composition (hereinafter referred to as "10S1Y"), the oxide ion conductivity at 1000 °C and 800 °C were 0.304 S/cm and 0.104 S/cm, respectively. In addition, in the case of the ScSZ sintered body having 10 mol% Sc_2O_3 - 1 mol% CeO_2 - 89 mol% ZrO_2 composition (hereinafter referred to as "10S1Ce"), the oxide ion conductivity at 1000 °C and 800 °C were 0.343 S/cm and 0.130 S/cm, respectively.

【0047】

(Example 2)

According to the following procedure, an SOFC was prepared. First, a binder was added to an 11S1A powder to give slurry and a green sheet was prepared by the doctor blade method. Then, this green sheet was sintered at 1600 °C for five hours to obtain an electrolyte sheet.

【0048】

Then, nickel oxide (NiO) and 10S1Y were weighed at

the weight ratio of $\text{NiO}:\text{10S1Y} = 4:6$, blended with a ball mill for 24 hours, and then dried. The binder was added to this fuel electrode material, which was then applied to one face of the electrolyte plate by the screen printing method, and sintered at 1300°C to give a fuel electrode. In addition, NiO is reduced to Ni by supplying hydrogen at the time of a generating test and acts as a catalyst.

【0049】

Next, $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (hereinafter referred to as "LSM") and 8YSZ were weighed at the weight ratio of $\text{LSM}:8\text{YSZ} = 8:2$, blended with a ball mill for 24 hours, and then dried. The binder was added to this air electrode material, which was then applied to the other face of the electrolyte sheet by the screen printing method, and sintered at 1150°C to give an air electrode. In addition, both sides of the electrode of the electrode electrolyte assembly were sandwiched between gas separators to obtain the SOFC.

【0050】

(Example 3)

Except that 10S1Ce was used as a ceramics component which is added to the fuel electrode, the SOFC was prepared according to the procedure similar to Example 2.

【0051】

(Comparison Example 1)

Except that 8YSZ was used as a ceramics component which is added to the fuel electrode, an SOFC was prepared according to the procedure similar to Example 2.

【0052】

A generating test was performed using the SOFCs obtained in Examples 2 and 3, and Comparison Example 1. A generating temperature was 1000 °C. In addition, fuel gas was humidified to predetermined humidity by passing through a bubbling vessel heated with an oil bath. Furthermore, overvoltage (electrode resistance) was measured by the ac impedance method.

【0053】

Fig. 2 shows the relation between current density and overvoltage when hydrogen is supplied to the fuel electrode and oxygen is supplied to the air electrode. Overvoltage increased more in the SOFC in Comparison Example 2 using Ni-8YSZ as the fuel electrode than in the SOFC of Example 2 using a cermet of Ni and 10S1Y (hereinafter referred to as "Ni-10S1Y") and the SOFC in Example 3 using a cermet of Ni and 10S1Ce (hereinafter referred to as "Ni-10S1Ce"). This result shows that the catalytic activity against hydrogen of the fuel electrode using ScSZ is higher than that of the fuel electrode using YSZ.

【0054】

Moreover, Fig. 3 shows the relation between current density and overvoltage when humidified methane whose S/C ratio is 0.03 was supplied to the fuel electrode and oxygen was supplied to the air electrode. In the case of Comparison Example 1 using Ni-8YSZ as the fuel electrode, the overvoltage reached about -100 mV when the current

density was about 0.5 A/cm^2 . In the region where the current density was 0.5 to 3 A/cm^2 , the overvoltage became approximately constant, and when the current density was more than 3 A/cm^2 , the overvoltage again tended to increase.

【0055】

In the case of Comparison Example 1, it is considered that the overvoltage rapidly increased in a low current density region since the reaction on the fuel electrode surface became a rate-determining process because of a very low S/C ratio in fuel. In addition, it is considered that the overvoltage again tended to increase in a high current density region since a process in which a gas component diffused through the fuel electrode became a rate-determining one due to an increase in fuel consumption, which appeared as the internal resistance of an electrode.

【0056】

On the contrary, in the case of the SOFC in Example 2 using Ni-10SiY as the fuel electrode, overvoltage was small as a whole compared with Comparison Example 1 and the overvoltage was about -60 mV when current density was about 0.5 A/cm^2 . In addition, in the region where the current density is 0.5 to 2 A/cm^2 , the overvoltage became approximately constant, and when the current density was more than 2 A/cm^2 , the overvoltage tended to decrease.

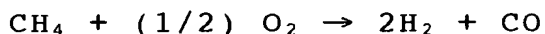
【0057】

It is considered that the overvoltage in Example 2 was smaller than that in Comparison Example 1 in low

and medium current density regions because the steam reforming reaction of methane proceeded independently by using Ni-10S1Y having high oxide ion conductivity for the fuel electrode, and the reaction on the fuel electrode surface thereby resisted being a rate-determining process. In addition, it is considered that the overvoltage of Example 2 conversely decreased in a high current density region because, as the catalytic activity of the fuel electrode against the reforming reaction of methane is high and as the partial oxidation reaction of methane expressed as the following Chemical Formula 4 takes place at the same time due to the oxide ions supplied through the second solid electrolyte, the reforming reaction of methane was promoted as compared with Comparison Example 1 and the internal resistance of the electrode was decreased.

【0058】

【Chemical Formula 4】



【0059】

In the case of the SOFC in Example 3 using Ni-10S1Ce as the fuel electrode, although the overvoltage in a medium current density region of 1 to 2 A/cm² increased to values approximately equal to those in Comparison Example 1, the overvoltage in low and high current density regions showed a tendency approximately similar to that in Example 2. The cause for increase in overvoltage in the medium current

density region, of which the details are not clear, is considered as a problem in a manufacturing process, but it was confirmed that generating performance better than that in Comparison Example 1 was shown at least in low and high current density regions.

【0060】

Moreover, Fig. 4 shows the relation between current density and overvoltage when humidified methane whose S/C ratio is 0.25 was supplied to the fuel electrode and oxygen was supplied to the air electrode. In the case of the SOFC in Comparison Example 1 using Ni-8YSZ as the fuel electrode, the overvoltage monotonously increased as the current density increases. On the other hand, in the case of the SOFC in Example 2 using Ni-10S1Y as the fuel electrode, the overvoltage became small as a whole compared with Comparison Example 1. In addition, the overvoltage conversely tended to decrease in the high current density region.

【0061】

It was found from the above results that if ScSZ is used as a fuel electrode material, the catalytic activity against hydrogen is improved. In addition, it was found that if methane is used as fuel, by the occurrence of not only the steam reforming reaction but also the partial oxidation reaction of methane, the reforming reaction of methane becomes active and the overvoltage decreases.

【0062】

(Example 4)

A 250-hour durability test was performed using the SOFCs prepared in Examples 2 and 3, and Comparison Example 1. The operating temperature of the SOFCs was 1000 °C. In addition, humidified methane whose S/C ratio is 0.03 was used for fuel. Furthermore, the current density was maintained at 0.75 A/cm² and the time course changes in output voltage were measured. Fig. 5 shows the results of the durability test.

【0063】

In the case of the SOFC in Comparison Example 1 using Ni-8YSZ for the fuel electrode, the output voltage at the early stage of operation was approximately equal to the SOFCs in Examples 2 and 3, and good initial characteristics were obtained. However, the output voltage decreased with a lapse of operating hours. Fig. 6 shows the time course changes in the current density and overvoltage measured for the SOFC in Comparison Example 1. It is found from Fig. 6 that in the SOFC in Comparison Example 1, the overvoltage with respect to the same current density increased with the course of time. It is considered that this is because carbon was deposited on the fuel electrode surface and the catalyst was poisoned by carbon through operating for many hours under a low S/C ratio condition.

【0064】

On the contrary, in the case of the SOFC in Example 2 using Ni-10S1Y for the fuel electrode, the time course

changes in the output voltage was slight. In addition, in the case of the SOFC in Example 3 using Ni-10S1Ce for the fuel electrode, there was little time course change in the output voltage even after 250-hour operation in which internal reforming was performed. This result shows that the catalyst of the fuel electrode is not poisoned by carbon even under a condition of a S/C ratio of less than 1.0 through using ScSZ as an electrode material, and stable power generation is possible. Moreover, it is shown that even if internal reforming power generation was performed for many hours, there was no time course degradation of the fuel electrode and no degradation of the catalytic activity of the fuel electrode.

【0065】

The preferred embodiments of the invention has been described in detail; however, it is not intended to limit the invention to the precise form disclosed at all, and various modifications are possible within the scope of the present invention.

【0066】

For example, although the SOFC according to the present invention is especially suitable as the internal reforming type SOFC, the application range of the present invention is not limited to the above-mentioned embodiments, and the present invention can also be applied to an SOFC using pure hydrogen or reformed gas for fuel in a similar way. In addition, as well as methane, liquid

fuel such as propane, butane, or alcohol can also be used as fuel.

【0067】

【Advantage of the Invention】

The present invention has the advantage that, as a cermet of a catalyst and the second solid electrolyte having high oxide ion conductivity is used as the fuel electrode of a solid oxide fuel cell, there is no poisoning by carbon, and stable power generation is ensured even if internal reforming power generation is performed under a condition of a low S/C ratio. In addition, it has the advantage that the catalytic activity of the fuel electrode is improved, enhancing the generating performance of the solid oxide fuel cell. Moreover, it has the advantage that there is little time course degradation of the catalytic activity of the fuel electrode even if internal reforming power generation is performed for many hours, which makes it possible to obtain the solid oxide fuel cell having excellent durability and reliability.

【BRIEF DESCRIPTION OF THE DRAWINGS】

【FIG. 1】

Fig. 1 is a schematic diagram of the power generating reaction of the internal reforming type SOFC.

【FIG. 2】

Fig. 2 is a view showing the relation between current density and overvoltage when hydrogen is supplied as fuel to SOFCs whose fuel electrode materials are mutually

different.

【FIG. 3】

Fig. 3 is a view showing the relation between current density and overvoltage when humidified methane whose S/C ratio is 0.03 is supplied as fuel to the SOFCs whose fuel electrode materials are mutually different.

【FIG. 4】

Fig. 4 is a view showing the relation between current density and overvoltage when humidified methane whose S/C ratio is 0.25 is supplied as fuel to the SOFCs whose fuel electrode materials are mutually different.

【FIG. 5】

Fig. 5 is a view showing the results of the durability test on the SOFCs whose fuel electrode materials are mutually different.

【FIG. 6】

Fig. 6 is a view showing the time course changes of the overvoltage when humidified methane whose S/C ratio is 0.03 is supplied as fuel to the SOFC using Ni-8YSZ for the fuel electrode.

【FIG. 7】

Fig. 7 is a view showing the schematic configuration of the SOFC.

【Explanations of Letters or Numbers】

- 10 a solid oxide fuel cell (SOFC)
- 12 an oxide ion conductive solid electrolyte (first solid electrolyte)

- 14 a fuel electrode
- 16 an air electrode
- 18 an electrolyte electrode assembly

【Document Type】 Abstract

【Summary】

【Purpose】 To provide a solid oxide fuel cell in which catalytic activity of a fuel electrode is high, and in which no poisoning by carbon occurs even when internal reforming is performed under a condition of a low S/C ratio, and further in which the time course degradation of the fuel electrode is reduced at the time of the internal reforming.

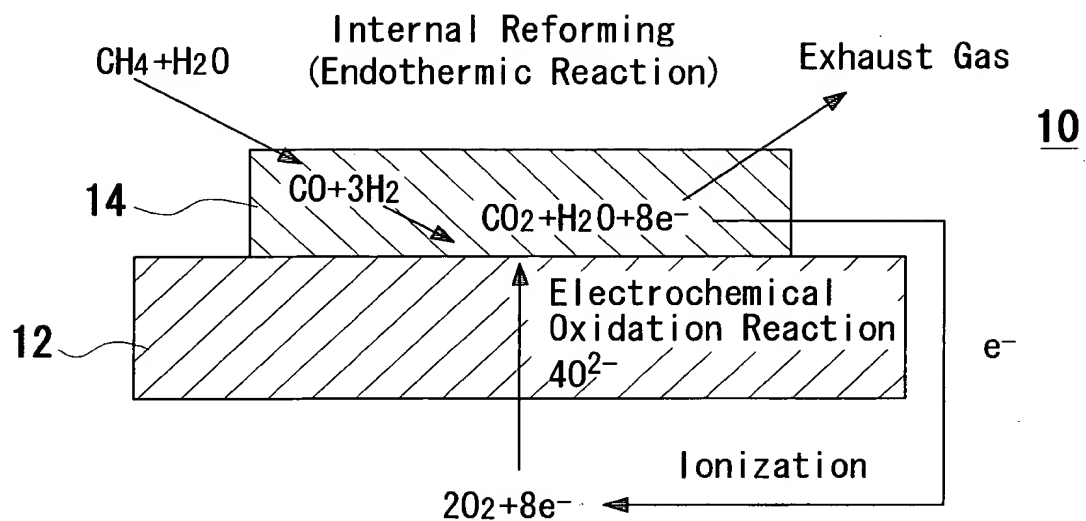
【Means for Solving Problem】 In a solid oxide fuel cell 10 having an oxide ion conductive solid electrolyte 12, and a fuel electrode 14 and an air electrode 16 connected to both faces thereof, a cermet of a catalyst and the second solid electrolyte whose oxide ion conductivity at 1000 °C is more than or equal to 0.2 S/cm is used as the fuel electrode 14. More specifically, it is preferable that the second solid electrolyte is scandia-stabilized zirconia (ScSZ) containing 9 to 12 mol% of scandia. In addition, the second solid electrolyte may further be ScSZ containing less than or equal to 2 mol% of yttria or ceria. Furthermore, the second solid electrolyte may be a composite material of ScSZ and less than or equal to 2 wt% of alumina.

【Chosen Drawing】 FIG. 5

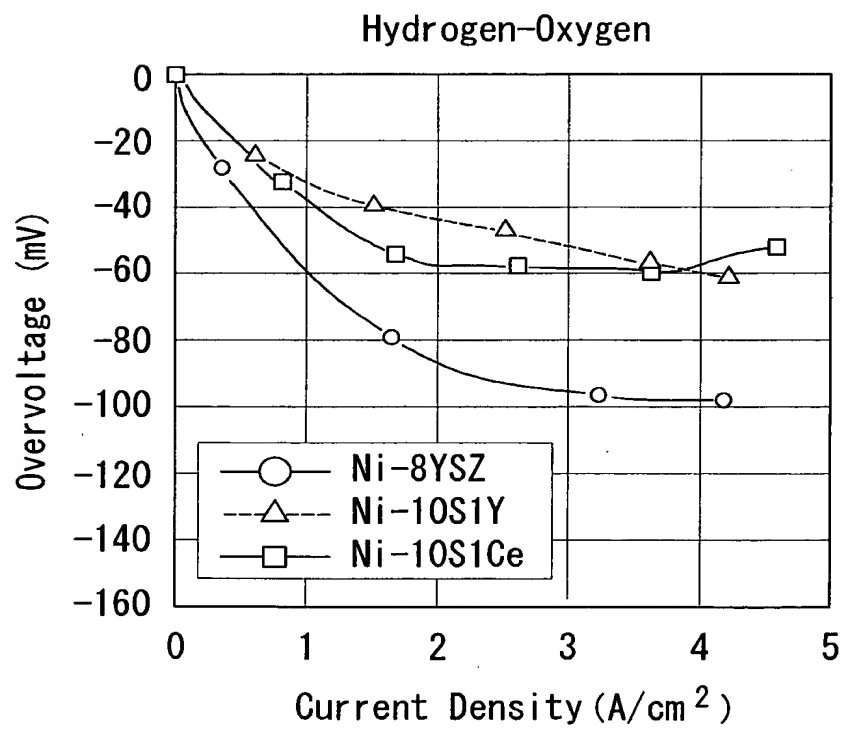
【Document Type】

Drawings

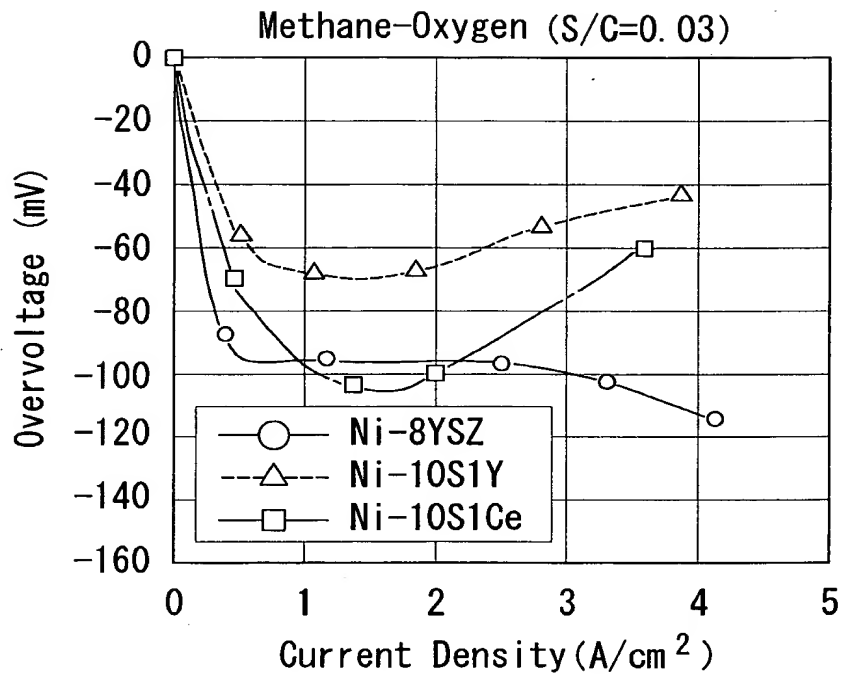
【FIG. 1】



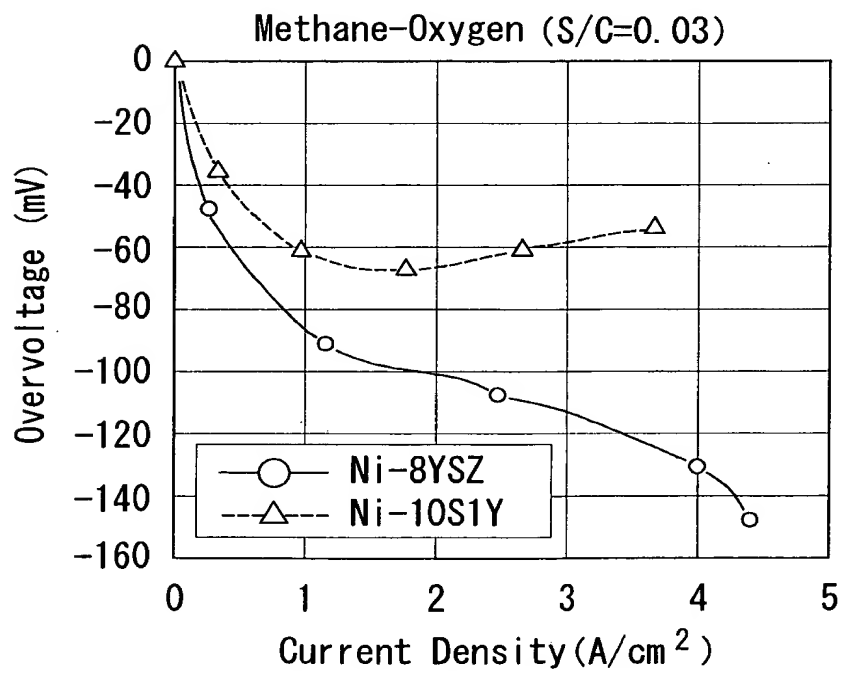
【FIG. 2】



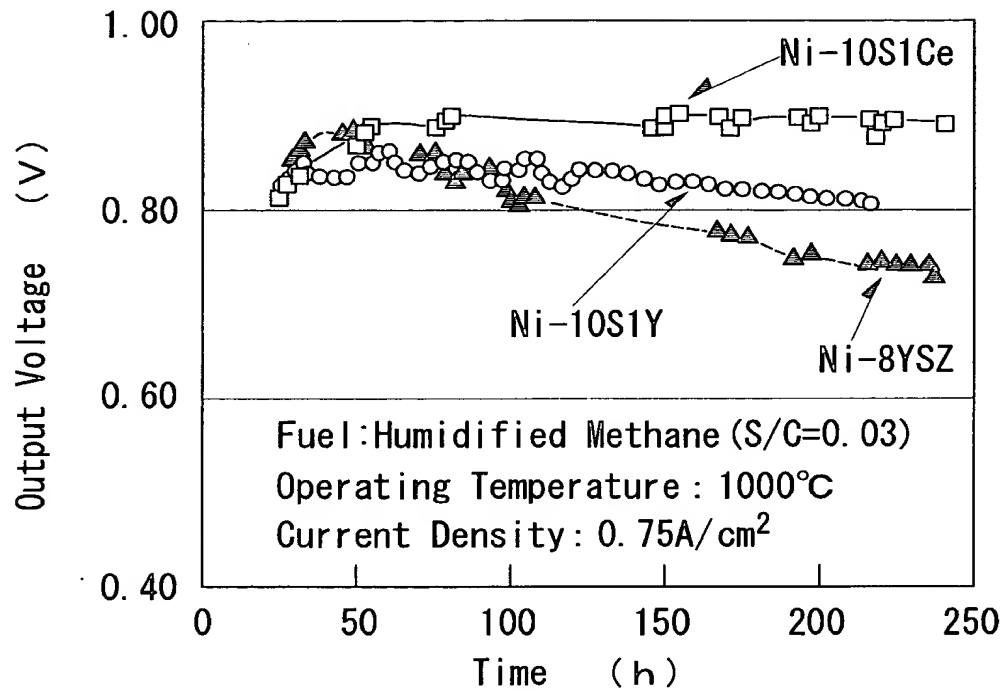
【FIG. 3】



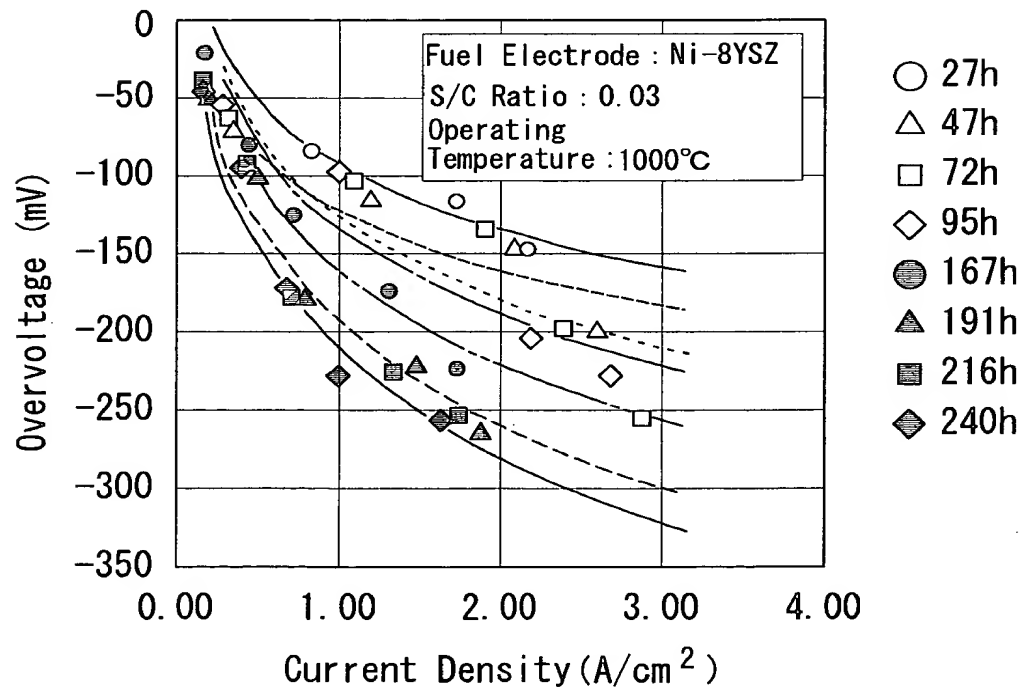
【FIG. 4】



【FIG. 5】



【FIG. 6】



【FIG. 7】

